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SYNTHESIS OF INDIUM PHOSPHIDE.(U)

N. KLAUSUTIS, ET AL.

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ROME AIR DEVELOPMENT CENTER
GRIFFISS AIR FORCE BASE, NEW YORK

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Synthesis of Indium Phosphide

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Indium phosphide is a compound of great interest both as a III-V semiconductor and as a substrate material for epitaxy. It is a difficult material to synthesize with sufficient purity. Techniques reported here appear to have solved the synthesis problem, and have produced high-purity material in sufficient quantity for the growth of single crystals. They may also be applicable to the synthesis of other III-V compounds. There remains a problem that must be solved before the method is considered reliable: explosions occasionally occur during product cooling.

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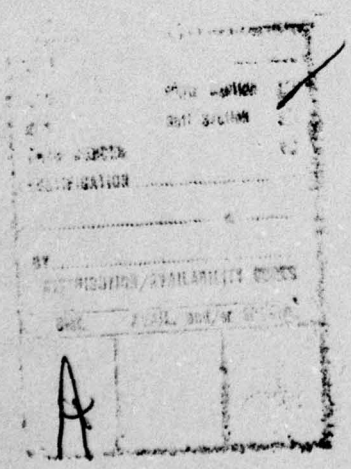

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1. INTRODUCTION

Indium phosphide is a compound with possible Air Force applications in two different fields of interest. As a semiconductor of the III-V group with a large (1.35 eV) band gap and high electron mobility, it has great potential as a substrate for device fabrication by epitaxial deposition. Thin film InP substrate device structures have great promise for: (1) integrated optics applications to replace conventional circuitry in Air Force airborne, satellite, and terrestrial communications systems to effect improvements in bandwidth, security, and immunity to electromagnetic interference, and (2) high frequency microwave device structures. Indium phosphide, however, is difficult to synthesize with sufficient purity for either application. Techniques developed in this laboratory now appear to have solved the synthesis problem and have produced high-purity material in sufficient quantity for the growth of crystals, but one problem remains: explosions sometimes occur during product cooling. The techniques may also be applicable to other semiconductors of the III-V group.

(Received for publication 4 October 1976)

2. BACKGROUND

Indium phosphide can be synthesized either by direct reaction of elemental phosphorus with elemental indium, or by reactions involving compounds of these elements. The direct reaction has an advantage in that high-purity elements can be obtained and there is no possibility of contamination by other reactants or products. It has a disadvantage in that the reaction is highly exothermic and can lead to a rapid, even catastrophic, buildup of pressure. A number of investigators[1-5] have, therefore, used various reactions involving compounds, but the resulting indium phosphide has often been insufficiently pure for the growth of good single crystals.

One method of direct reaction of the elements consists of mixing phosphorus with molten indium and allowing them to react. This reaction is highly exothermic, generates very high pressures, and must be carried out in a pressure bomb. An alternative approach[6-8] entails transporting phosphorus in the vapor phase from a stock of solid phosphorus in one region of an ampule to a stock of indium in a thermally isolated region; this method allows a reaction to occur at a controlled rate without overheating the large mass of phosphorus. This approach was modified for use in the present investigation. Previous attempts to use this sort of direct reaction have been limited to the production of small quantities of InP; scaling up such processes in this laboratory has resulted in several explosions (equipment was damaged but no injuries resulted). In the present method, catastrophic pressure buildup during synthesis is avoided by establishing a steep temperature gradient in the solid phosphorus to limit the amount that is hot enough to vaporize. A thorough understanding of the chemical and physical properties of all components of the system is essential for the safe production of InP by this technique.

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2. Garton, G., and Powell, H. M. (1957) J. Inorg. Nucl. Chem., 4:84.
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8. Shafer, M., and Weiser, K. (1957) J. Phys. Chem., 61:1424.

3. PROPERTIES OF PHOSPHORUS

Phosphorus occurs in several allotropic forms. At atmospheric pressure and room temperature it can exist as crystalline white phosphorus or as amorphous red phosphorus. White phosphorus is extremely reactive and poisonous and is likely to burst spontaneously into flame in the presence of oxygen. Red phosphorus is considerably less reactive and less toxic, but it must, nevertheless, be handled carefully. White phosphorus melts at about 50°C to a liquid that resolidifies to red phosphorus at approximately 300°C. The vapor pressure of this liquid does not exceed about 1000 torr, too low to use for vapor transport.[9] Red phosphorus remains solid from room temperature to approximately 600°C, at which point it melts to a clear, straw-colored liquid. The vapor pressure of this liquid increases very rapidly with increasing temperature (from approximately 50 atmospheres at the melting point) and is too high for laboratory glassware. Therefore, liquid phosphorus cannot be used.

Since there is no advantage, and several disadvantages, to the use of white phosphorus, red phosphorus was chosen for these experiments. It was similar to that whose vapor pressure is given[10] by

$$\log_{10} P = - 6070/T + 8.67$$

where T is the temperature in °K and P is in atmospheres. A later reference[11] apparently applies to phosphorus in somewhat different forms. The earlier reference (Reference 9) was therefore used. Values of P vs T, with T expressed in °C, are plotted in Figure 1. Red phosphorus at 500°C has a vapor pressure of 6.57 atmospheres. At 540°C the vapor pressure is 15.99 atmospheres.

The technique reported here consists of heating solid red phosphorus and solid indium to different temperatures in separate sections of a long tube, or ampule, and controlling the position of the phosphorus in a region of the ampule where there is a large temperature gradient, to provide sufficient vapor pressure to drive the reaction

$$4\ In + P_4 \leftrightharpoons 4\ InP$$

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9. Van Wazer, J. R. (1958) Phosphorus and Its Compounds, Vol. 1, Interscience Publ. Inc., New York, p. 101.
10. Van Wazer, J. R. (1958) Op. Cit., p. 117.
11. Bachmann, K. J., and Buehler, E. (1974) J. Electrochem. Soc., 121:835.

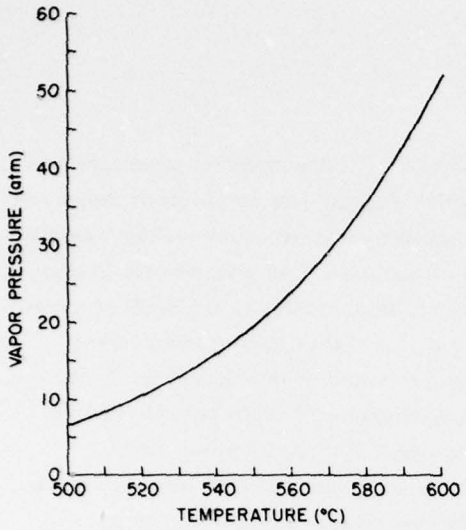

Figure 1. Vapor Pressure of Solid Red Phosphorus

in the direction of indium phosphide without exceeding the pressure limit of the ampule. The indium, which melts at about 156°C, must be maintained at a temperature higher than that of the phosphorus to prevent condensation of phosphorus at the indium end of the tube. If the indium is maintained at a temperature below about 1070°C, the melting point of InP, the product will precipitate as a powder, trapping some indium on its surface and preventing complete reaction. It is, therefore, preferable to heat the indium above this temperature, but not to exceed 1100°C, since above that temperature the quartz ampule begins to devitrify significantly, and there is a risk of its cracking upon cooling.

The vapor pressure of phosphorus from InP at its melting point has been variously reported between 5 and 60 atmospheres.[12,13] The value of 6 atmospheres is used in calculating the amount of phosphorus in excess of stoichiometry with which to charge the system. Using as starting materials "teardrops" of indium and chunks of red phosphorus, both 6N pure, reactions are routinely run to 99 percent completion in 48 hr or less, yielding 70-g batches of InP. The "hot" and "cold" ends of the ampule are maintained at approximately 1100°C and 500°C, respectively. The phosphorus must be carefully selected to insure that it contains no white phosphorus, in order to avoid spontaneous combustion during handling. The red phosphorus provided by various suppliers differs markedly in quality in this respect: red phosphorus deposited in a layer on the ampule is inferior to that supplied in chunks. The phosphorus (purity 6N) used successfully in this investigation was purchased from Alfa Inorganics, Beverly, Massachusetts. Indium (purity 6N) was obtained from the Indium Corporation of America, Utica, New York.

12. Weiser, K. (1957) J. Phys. Chem., 61:513.
13. Van den Boomgaard, J., and Schol, K. (1957) Philips Res. Reports, 12:127.

4. SYNTHESIS

The chunks of phosphorus are placed in a mortar under an inert atmosphere and ground with a pestle. About 15.5 g of the resulting powder is placed in the closed end of the quartz ampule, which is about 80 cm long, has a 10 mm inside diameter, and a 3 mm wall thickness. The ampule is constricted to an inside diameter of 6 mm near its center, and it is necessary to grind the phosphorus so it will pass this constriction.

With the ampule in the vertical position, approximately 55 g of indium is placed in the section of the tube above the constriction, which is blocked by a larger piece of red phosphorus to keep the indium out of the lower section. Figure 2 shows the ampule loaded with the reagents. The masses chosen provide for stoichimetry plus 6 atmospheres overpressure of P_4 vapor in the available volume of the ampule. Phosphorus vapor occurs as P_4 below 800°C, with increasing admixtures of P_2 at higher temperatures.[14] The available volume of the ampule changes very little as the reaction proceeds, as the volume of the InP, at a density of 4.81 g/cm^3, matches that of the indium and phosphorus, with densities of 7.53 and 2.2 g/cm^3 respectively, almost exactly.

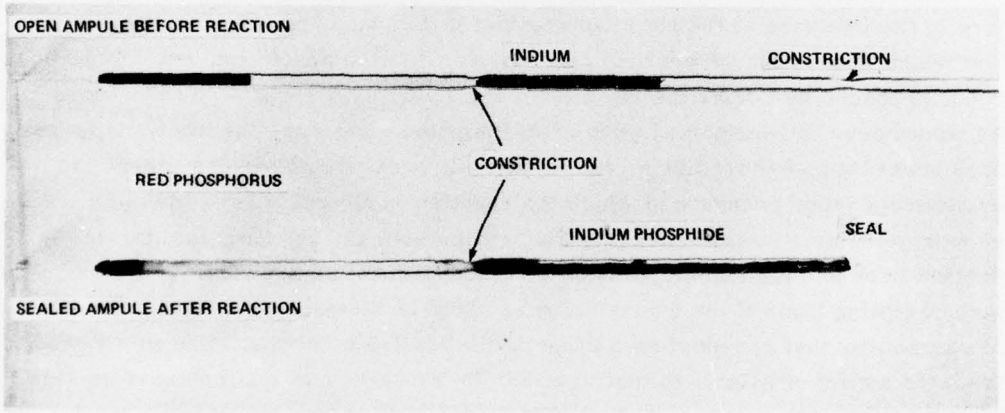

Figure 2. Indium Phosphide Synthesis Ampules Before and After Reaction

The tube is next evacuated and sealed off, leaving the indium and phosphorus in equally long sections, with a constriction between them that will permit the flow of vapor but prevent the passage of liquid between sections when the ampule is horizontal. The chunk of phosphorus initially in the indium end will

14. Van Wazer, J.R. (1958) Op. Cit., p. 95.

react or vaporize safely as the tube is heated. The tube is placed in a horizontal two-zone furnace, with the end containing the phosphorus extending 7 cm out of the furnace. The indium end, or hot end, of the furnace is now heated gradually to 1100°C, while the phosphorus end, or cold end, is heated to about 800°C, but kept below the temperature of the hot end at all times. The temperatures are measured by control thermocouples about 30 cm from the hot end and 20 cm from the cold end of the furnace. A third thermocouple (monitoring thermocouple) is inserted at the cold end to locate the 500°C point. As the temperature rises, the phosphorus in the warmer part of the ampule vaporizes and redeposits at the cold end. This process insures that, so long as there is a surface below 500°C, no appreciable amount of phosphorus will be above 500°C, and there will be no danger of explosion. The initial extension of the ampule out the cold end of the furnace provides sufficient volume below 500°C for all the phosphorus. As the redeposition proceeds, the ampule is pushed into the furnace to keep the leading edge of the phosphorus at about 500°C. This process may take several hours. When it is complete, a distinct interface will exist at about the 500°C isotherm and at a pressure in the ampule of about 6 atmospheres. Figure 3, the temperature profile of the furnace under the stated operating conditions, shows that there is a strong (50C°/cm) thermal gradient at this isotherm.

The vapor pressure of phosphorus in the ampule is determined by the temperature of the interface at the phosphorus end. If this vapor pressure is greater than that which would result from the presence of InP in the molten indium, the excess vapor pressure will drive the reaction of indium with phosphorus to form more InP. As phosphorus is transported away from the phosphorus end, the interface moves back toward a cooler isotherm, and the driving pressure decreases toward the equilibrium vapor pressure at which the reaction would cease. To maintain the reaction, the ampule is pushed into the furnace until the phosphorus interface is brought back to a higher temperature and a consequent higher vapor pressure. The safe operating limit of the quartz ampule, about 20 atmospheres, limits the amount of phosphorus that can exist as a vapor in the available volume. The worst case, from the aspect of safety, is that in which the reaction with the indium is so slow and the vaporization so fast that all phosphorus in the increment of the ampule pushed into the furnace instantly appears as vapor. In this case, for the given experimental circumstances and assuming ideal gas behavior, the pressure will be increased by about 20 atmospheres for each cm of insertion beyond the 500°C isotherm. A 5 mm increment of insertion will produce only a 10 atmosphere increase in ampule pressure to a total of 17 atmospheres, which is well within safe operating limits for the quartz ampules.

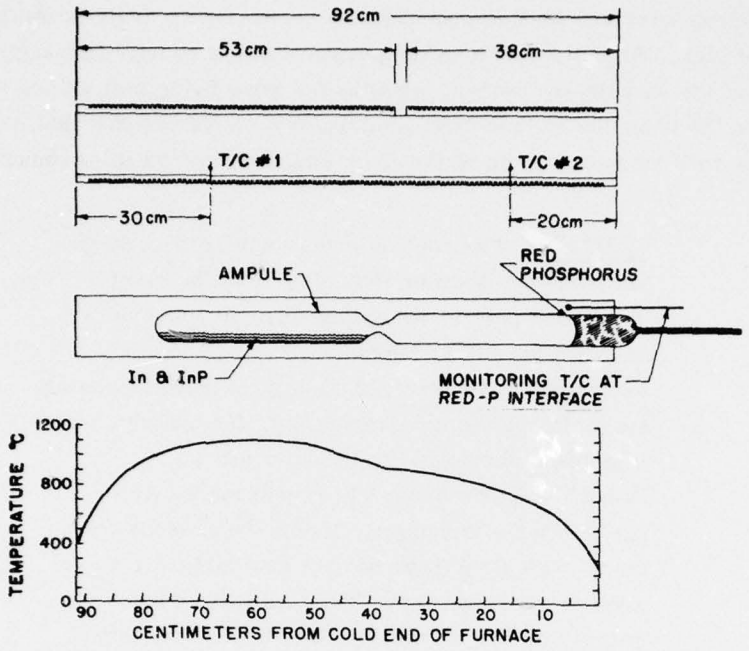

Figure 3. Indium Phosphide Synthesis Furnace With Reaction in Progress

With the phosphorus fully compacted and the interface at 500°C, the ampule is pushed 5 mm into the furnace, allowing the reaction to proceed. Depending on the completeness of the reaction prior to repositioning the ampule, the receding interface will again approach the 500°C point in 1/2 hr to 2 hr. This process is periodically repeated until most of the phosphorus has been consumed. The end of reaction can be detected by the failure of the interface to recede following an increment of motion of the ampule. Generally, if the interface does not move after 2 hr, it will not move with greater times. A similar effect may occur early in the run if a blockage is formed in the ampule. Due to slight geometric irregularities in ampules and furnace cores, manipulating the ampule may cause some of the In-InP melt to flow to a cool region of the ampule, where the melt freezes quickly, forming a blockage to vapor flow. After all the indium on the phosphorus side of the blockage has reacted, the reaction ceases. If this occurs, the run should be terminated at this point as if it had been successfully completed. Attempting to force the reaction by additional insertions of the ampule into the furnace will result in an explosion.

When the reaction has been completed, the furnace is slowly cooled by first reducing the hot zone temperature at a rate of 50 to 100C°/hr, while maintaining

the phosphorus interface stationary. This is necessary to avoid decomposition of the InP product. When the hot zone temperature drops to approximately 550°C, both ends of the ampule are cooled, with the hot zone being maintained slightly higher than the phosphorus interface temperature. This insures that excess phosphorus will condense in the phosphorus end, leaving the InP product free of excess P.

> CAUTION: The cooling process from the reaction temperature down to about 700°C is the most dangerous part of the synthesis, for reasons that have not yet been determined. A number of explosions have resulted during cooldown, causing some damage to equipment, but, fortunately, no injuries to personnel in the laboratory. Hsieh[15] reports about 30 percent mortality in his synthesis technique. While the reasons for these explosions have not yet been determined, a number of factors have been eliminated by comparing the technique described in this report with Hsieh's technique.

Explosions are not the result of: (1) failure to control the vapor pressure of the phosphorus, or explosions would occur during heating and initial reaction; (2) attack on quartz by the In-InP melt, since Hsieh experienced explosions with vitreous carbon boats; (3) defective ampules, which would fail earlier in the cooldown cycle; (4) rate of cooling, since Hsieh cooled at 3 to 4 C°/hr, while 50 to 100 C°/hr rates were used in this work.

5. CONCLUSIONS AND RECOMMENDATIONS

Indium phosphide has been successfully synthesized by the technique described. No incidents occurred during the synthesis. However, the explosion problem during cooldown has not been successfully resolved, because the synthesis effort was terminated before a solution was achieved.

Equipment damage can be minimized by using a special liner inside the furnace to contain explosion fragments. In the event of any future InP synthesis and crystal growth programs, this problem must be addressed first. Any proposals dealing with synthesis should clearly indicate how this problem will be solved.

15. Hsieh, J. (1976) Private Communication.

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